

Influences of Large Polymer Particles on Lamellar Microdomains of Block Copolymer

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1 Introduction

A block copolymer with incompatible components self-assembles into microphase-separated structure highly ordered with a nm scale in bulk. So far the microphase-separated structures for block copolymers with different molecular architectures and their blends with homopolymers have been well investigated to control the morphology of polymer multicomponent systems.

In this study, the effects of large polymeric particle on phase-separated structure of block copolymer were investigated by using small-angle X-ray scattering.

2 Experiment

A diblock copolymer with polystyrene (PS) and 1,4-addition rich poly(isoprene) (PI), purchased from the Polymer Source Inc., was used. Its number-averaged molecular weight was 225×10^3 , and the volume fraction of PS block chain was 0.49. The polymer particles (Sekisui Chemical Co., Ltd.), synthesized by cross-linking divinylbenzene, with different diameters of 3 and 30 μm were used. The film specimens were prepared by solvent casting from dilute solutions of PS-block-PI with 0-30 wt% particles in toluene, and then annealed at 150°C for 24 hours in a vacuum.

SAXS measurements were performed on BL-6A with X-ray having the wavelength, λ , of 0.154 nm. The camera length was about 2.5 m, and PILATUS was used as a detector. The SAXS was observed in the edge-view geometry, in which X-ray beam is irradiated along the direction parallel to the film surface.

3 Results and Discussion

Fig.1 compares two-dimensional SAXS patterns for PS-block-PI with and without 10 wt% of the polymeric particles having the diameter of 3 μm . The solvent-cast film of the parent diblock copolymer exhibited a highly anisotropic pattern elongated along the horizontal direction in the figure. This suggests that the lamellar microdomain oriented parallel to the film surface is thinner than that with the perpendicular orientation in the film. The scattering intensity profile, $I(q)$, as a function of the scattering vector, q ($=(4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle), was obtained by sector-averaging the scattering pattern at $\pm 5^\circ$ around every 5° from 0° to 90° in the azimuthal angle, ϕ . The thicknesses, D , of the lamellar microdomains oriented parallel and perpendicular to the film surface were evaluated to be about 99 and 107 nm from the profiles at ϕ of 0° and 90° , respectively. On the other hand, the SAXS pattern for PS-block-PI with the particles was less anisotropic. The D values for the parallel and perpendicular lamellae were almost the same,

and comparable to that for the perpendicular one of PS-block-PI without the particles.

The degree of orientation, $\langle \cos^2\phi \rangle^{1/2}$, of lamellar microdomains relative to the film surface was evaluated following the previous study [1], and its dependence on the particle content is shown in Fig. 2 along with the D values evaluated for the profiles at $\phi=0^\circ$. $\langle \cos^2\phi \rangle^{1/2}$ decreased with increasing the particle content, and then increased after the minimum at 10 wt% of the particle. The D values were evaluated to be larger for the less oriented lamellae.

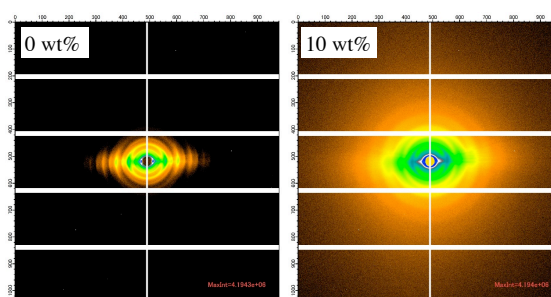


Fig. 1: The two dimensional SAXS patterns for a parent PS-block-PI (left) and its blend with 10 wt% of the polymeric particles having the diameter of 3 μm (right).

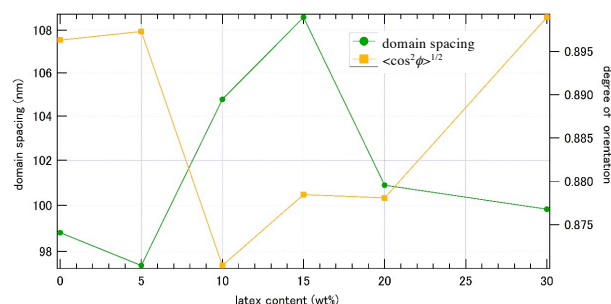


Fig. 2: The degree of lamellar orientation $\langle \cos^2\phi \rangle^{1/2}$ and domain spacing evaluated for the SAXS profile at $\phi=0^\circ$ as a function of the content of the polymeric particle.

Acknowledgement

SAXS measurement was partly supported by a Grant-in-Aid for Scientific Research (C) (24550252) of the Ministry of Education, Culture, Science, Sports and Technology, Japan.

Reference

[1] Y. Matsushita *et al.*, *Macromolecules* **23**, 4317 (1990).

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